HYDROGEN-OXYGEN RELAXATION
EFFECTS ON SPACECRAFT OPERATIONS IN THE
70 KM TO 100 KM ALTITUDE REGION

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THESIS

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ABSTRACT

Hydrogen and oxygen reactions in the earth's atmosphere between 70 Km and 100 Km may at times serve as a relaxation mechanism for this region of the atmosphere. Energy stored in this region as a result of intense solar radiation, or energetic particle bombardment, may be rapidly released by hydrogen-oxygen reactions. Such reactions include ion-ion recombination and condensation of supersaturated mixtures of water or hydrogen peroxide vapors in the region.

The possible nature of such mechanisms was considered in an attempt to estimate the effects on spacecraft performance in this altitude region. The basic question involved was whether the chemical and kinetic energy stored in hydrogen-oxygen complexes could materially affect spacecraft performance.

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I. INTRODUCTION

The potential energy stored in the earth's atmosphere in terms of the atomic and ionized species can at times result in substantial heating of spacecraft surfaces. This heating results from various mechanisms such as ion recombination at the vehicle surface, or by radiation from hot reacting gases near the vehicle.

Normally, the heat transferred by such reactions represents only a small fraction of the total heat load, since gas particle kinetic energy is a much greater source of thermal energy. However, in the upper regions of the atmosphere, where atomic oxygen is the predominate species, the chemical and internal energy released near a vehicle surface may exceed the total particle kinetic energy by a significant factor.

Similar potential energy storage and release mechanisms may also act in lower regions of the earth's atmosphere as a result of intense solar radiation and proton bombardment. The following discussion considers the probable nature of energy storage and relaxation mechanisms involving excited hydrogen and oxygen which may act in the altitude region from 70 Km to 100 Km known as the mesosphere. Particular attention is given to the buildup of an excited state, to possible relaxation mechanisms, and to some of the possible controlling factors in these reactions.

The primary reason for this investigation was to identify possible areas of spacecraft operation which may be adversely affected by a sudden relaxation of an excited atmospheric layer in the 70 Km to 100 Km

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region. The operational implications mentioned are mainly based on
reported vehicle effects from ionic or chemical mechanisms in highly
ionized environments.

Several operational alternatives are also mentioned with respect to
a proposed energy storage and relaxation cycle for this altitude region.
These recommendations are based solely on the avoidance of spacecraft
operation during periods of peak excitation in the specific areas
where such excitation is most likely to occur.

II. ENERGY STORAGE MECHANISMS

A. GENERAL

The principal energy source for atmospheric heating is solar radiation, primarily in the short ultra-violet wave lengths. Approximately two-thirds of the total atmospheric heating comes from this source [1][1]. The remaining energy absorbed by the earth's atmosphere comes from a complex interaction between the earth's atmosphere and energetic particles in the solar wind. This interaction and subsequent energy conversion is especially important because intermediate energy storage steps are often involved. These intermediate storage levels can lead to the formation of excited altitude regions of the earth's atmosphere. The following sections describe how protons from the solar wind can lead to formation of an excited energy level in the 70 Km to 100 Km region.

B. THE SOLAR WIND

The solar wind consists mainly of ionized hydrogen, protons and electrons, previously emitted from the surface of the sun during some type of solar disturbance. These protons and electrons form a tenuous plasma that moves radially outward from the sun at a velocity [2] of 300 Km/sec to 500 Km/sec with an average density of 10 ions/cm^3. The velocity and density of the solar wind vary with solar flare activity. This causes the relative solar wind as seen from the earth's orbit to vary both in direction and in intensity or magnetic pressure.

[1]Numbers in brackets refer to references listed on page 49

Internal magnetic field lines make the solar wind plasma behave like a fluid by communicating information between individual particles along these same field lines. Thus all the particles along a field line are constrained to move together in much the same way that collisions force neutral gases to follow streamlines. This analogy is useful in describing the interaction of the solar wind with the earth's magnetic field. The concepts of ordinary shock waves and resulting flow fields may be extended to include magnetic field interactions.

Early investigators [3] predicted the formation of a detached shock wave some distance from the earth, similar to the shock formed by a bluff body in ordinary hypersonic flow. The earth's magneto-hydrodynamic Mach number, M_A, is approximately eight [4] where

$$M_A = V_e/V_a \tag{1}$$

$$V_a = B/\sqrt{4\pi\rho} \qquad V_e = \text{earth's velocity} \tag{2}$$

$$B = \text{Magnetic Field Strength}$$

$$\rho = \text{Density.}$$

Evidence of such a detached shock was discovered by the IMP-I satellite launched in November 1963. IMP-I detected abrupt changes in the magnitude and direction of the magnetic field associated with the interaction of the solar wind and the earth's magnetic field. The magnetic field upstream from this discontinuity was found to be quiet and steady, while the magnetic field downstream was found to be disturbed and turbulent. The location [5] and width of the disturbed region are shown in Figure 1. The net result is basically two distinct flow fields: one for the interplanetary particles and another flow field associated with the earth itself. The flow field associated with the earth is generally known as the magnetosphere.
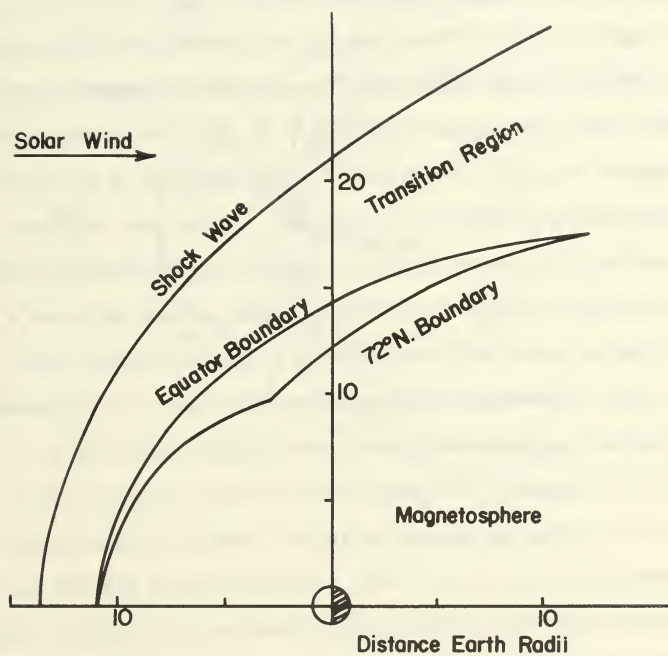
FIGURE I. LOCATION OF THE MAGNETOSPHERE BOUNDARY
AT THE EQUATOR PLANE AND AT 72° N. LAT.

Since the particles in the solar wind are constrained to follow magnetic field lines, most of these particles are deflected around the earth and therefore do not enter the magnetosphere directly. However, two important factors exist near the earth's polar axis which contribute to large scale entrapment of solar protons and electrons by the earth's magnetosphere or to large scale dumping of protons and electrons directly into lower regions of the atmosphere near the earth's poles. The basic factor [6] involved in this entrapment process is the distortion of the earth's magnetic field that results from an interaction of the earth's magnetic field with the solar wind. This distortion is most severe near the earth's polar axis as shown in Figure 2. The field lines in the magnetosphere are generally identified by the latitude at which the field line intersects the earth's surface. In this case the field lines near 80 to 85 degrees magnetic latitude are deflected in such a manner that solar particles can travel directly toward the earth's surface with no opposition from the earth's magnetic field. These regions of the magnetosphere represent neutral magnetic field points and the ambient particle density is generally much less than in stronger field regions. The magnetosphere tends to maintain this void region by collecting and redistributing all charged energetic particles that enter this neutral zone. Thus, particles such as protons and electrons from the solar wind may enter these neutral zones and travel directly to lower regions of the earth's atmosphere, 70 Km to 100 Km, or they may be collected and redistributed to other regions of the magnetosphere.
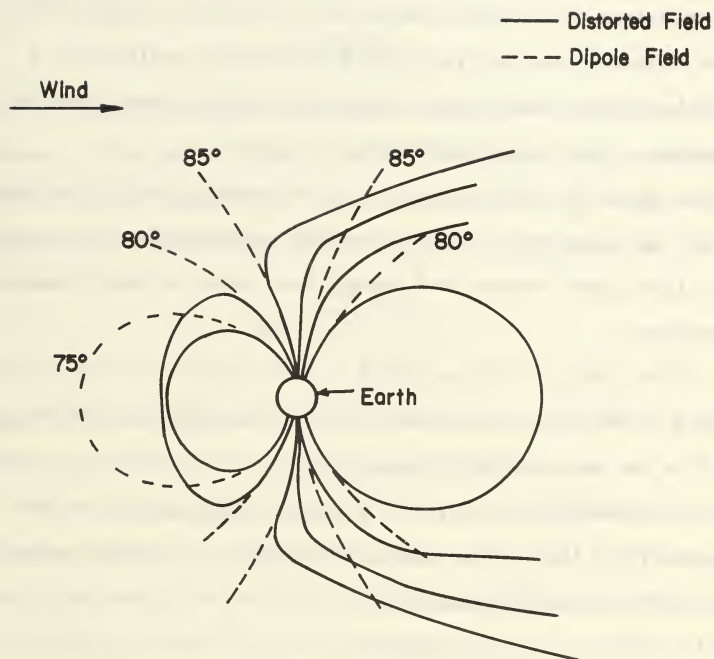
FIGURE 2. FIELD DISTORTION PRODUCED BY
THE SOLAR WIND

C. PARTICLE ENTRAPMENT IN THE MAGNETOSPHERE

The term magnetosphere is applied to those regions of the earth's outer atmosphere where particle behavior is governed primarily by the earth's magnetic field. Charged particle motion in the magnetosphere is constrained in an orderly manner about the earth's magnetic field lines so that collisional processes are treated as negligible. A particle tends to maintain its chemical and kinetic energy indefinitely throughout a vast region surrounding the earth.

The motion of charged particles in the magnetosphere [7] is unique in that any component of particle velocity perpendicular to the magnetic field lines results in a central force given by the following expression:

$$\overline{F} = q \ \overline{v} \ x \ \overline{B} \tag{3}$$

where q is the charge of the particle, $\overline{v}$ is the particle velocity vector and $\overline{B}$ is the magnetic field strength.

This induced force results in a helical motion along a central magnetic field line with an angular frequency, w, and helix radius, R, given by the following expressions:

$$w = q/M \ B \tag{4}$$

$$R = \frac{M}{q} \ V\perp/B \tag{5}$$

where M is the mass of the particle and $V_\perp$ is the perpendicular component of velocity.

The charged particle is free to move along the field lines under restrictive conditions. Kinetic energy must be conserved and, if the particle moves into a region of converging or diverging magnetic field

lines, the number of magnetic field lines, Φ, encircled by the particle
orbit must remain constant, i.e.:

$$d\Phi/dt = 0. \tag{6}$$

This invariant can be expressed in terms of a constant magnetic moment,
μ, given by

$$\mu = \frac{1/2 \ M \ V\perp^2}{B} . \tag{7}$$

As B increases, the rotational kinetic energy must increase at the
expense of longitudinal kinetic energy. Eventually all of the particles'
original kinetic energy will become rotational kinetic energy at a
specific point in the field given by the following expression

$$B_{max} = \frac{1/2 \ M \ V_o^2}{\mu} \tag{8}$$

where V_o is the original particle velocity. In the magnetosphere,
B_{max} represents the closest point of approach to the surface of the
earth for a particle of a specific kinetic energy.

The particle does not remain at this point of maximum field
strength. Instead, it reverses its course and travels back along the
field line, away from the point of field convergence. The reason for
this reversal is that a particle moving in a region of magnetic field
convergence, with a finite helix radius, experiences an unbalanced
longitudinal force as shown by a summation of forces around the helical
path. Work done against the field in moving toward the point of magnetic
field convergence is subsequently recovered during the particles motion
away from the point of field convergence.

In the magnetosphere a charged particle travels from one reflection
point, B_{max}, along a given field line to a conjugate reflection point

in the opposite hemisphere. In addition to this basic helical motion, there is some lateral drift due to the curvature of the magnetic field. The overall resulting motion is shown in Figure 3. Charged particles experiencing this type of motion are termed stably trapped. These particles as a group form the Van Allen radiation belts.

Charged particles may be trapped over a wide variety of energy levels and injection angles. In this discussion, we are concerned primarily with how particles from the solar wind are captured or trapped by the magnetosphere. Referring to Figure 2, the major distortions in the earth's magnetic field occur at distances of several earth radii, so that even a particle travelling through the neutral zone will eventually experience an increase in magnetic field strength as it approaches the earth. Once the magnetic field strength reaches the critical value necessary for reflection, the particle may become stably trapped (normally above 200 Km). On the other hand, higher energy particles may penetrate to altitudes where collisions (see Figure 4) become important, and the particle may be absorbed by the lower regions of the earth's atmosphere. Once a particle loses its electrical charge by collision, or if its velocity is decreased substantially, the magnetic forces are no longer effective in controlling the particle's motion. The particle then remains in the vicinity of the collision, and is no longer trapped by the magnetosphere.

Up to this point, the earth's magnetic field has been treated as stationary, however equations 1 through 8 apply to any relative motion between the particles and the magnetic field. This is important since the earth's magnetic field may oscillate at times and thereby impart
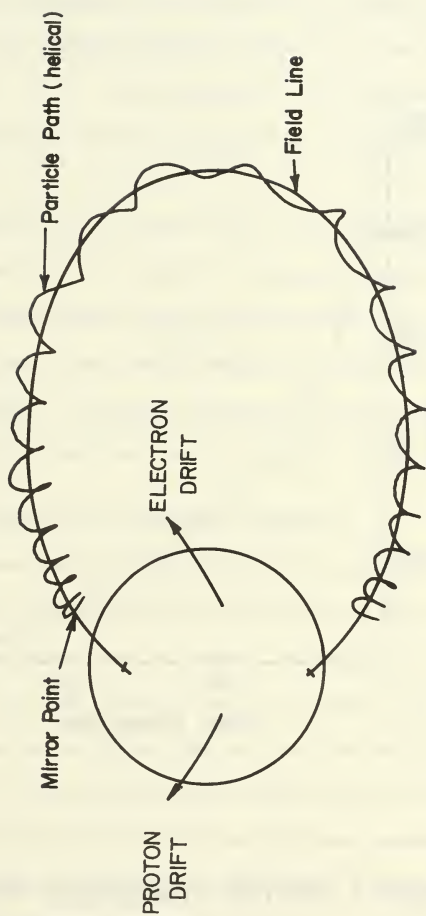
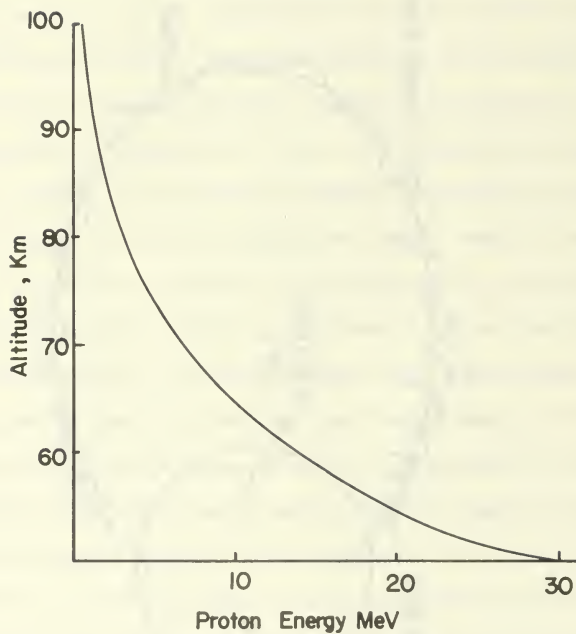FIGURE 3. MOTION OF CHARGED PARTICLES IN THE MAGNETOSPHERE

FIGURE 4. PROTON ATMOSPHERIC PENETRATION
         DEPTH (REF. 13, p.161)

additional energy to many of the trapped particles. This in turn, leads to lower reflection points with subsequent particle losses by increased collisions.

Thus, the lower atmospheric region receives energetic protons from two sources: either directly from the solar wind along the neutral field line surfaces, or by some disturbance in the magnetosphere which literally dumps [8] previously trapped protons into these lower regions (see Figure 5).

Energetic particles from high altitude nuclear explosions [9] are also trapped in much the same manner as energetic particles from the solar wind. The final energy deposition region for these trapped particles is governed by the same geomagnetic mechanisms discussed previously. Therefore, the energy deposition region's altitude, magnetic latitude and longitude can be reasonably well predicted.

D. ATMOSPHERIC ABSORPTION OF ENERGETIC PARTICLES

Energetic protons which penetrate the atmosphere to altitudes of 200 Km or less inevitably experience collisions and then become a part of this region in the form of neutral or excited hydrogen. Once such collisions occur, the magnetic forces no longer play a dominant role in controlling the particle's motion, and the particle will not be reflected out into the magnetosphere. The proton can only escape to higher altitudes by the action of some diffusion mechanism.

The incoming proton flux for the region below 200 Km reportedly exceeds the upward diffusion flux for hydrogen by a factor of two [10]. This suggests that a substantial number of these incoming protons remain at altitudes below 200 Km. Furthermore, there are no indications
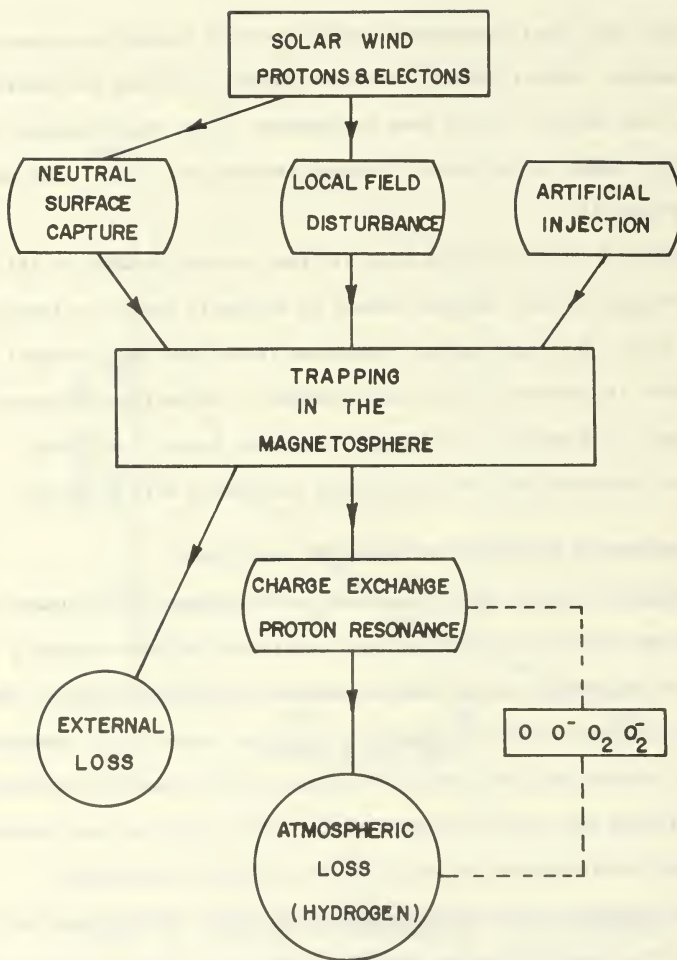
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FIGURE 5. "FLOW CHART" FOR ENERGETIC PARTICLES

that the hydrogen concentration increases in the region from 100 Km to 200 Km as a result of this proton invasion of the region. This implies that the protons themselves may directly penetrate to altitudes less than 100 Km, and that possibly some of the excited hydrogen produced by proton collisions above 100 Km diffuses downward to somewhat lower altitudes.

Direct proton penetration to altitudes less than 100 Km is a relatively straightforward process. The main requirement is sufficient initial particle energy to withstand a number of collisions above 100 Km. Generally, an initial particle energy level of 1 Mev is required for a vertically incident proton to reach 100 Km. The maximum penetration depth for protons with higher energy levels is shown in Figure 4.

Downward diffusion [11] of atomic or molecular hydrogen to lower altitudes is a complex process. The state and chemical composition of the region concerned are the important factors. In this respect, the altitude region from 70 Km to 100 Km has several unique physical and chemical [12] properties which must be considered. The 70 Km to 100 Km region of the earth's atmosphere is generally known as the mesosphere [13]. The mesosphere is basically a transition region between the neutral gases in chemical equilibrium at lower altitudes and the more ionized gases in diffusive equilibrium at higher altitudes. The primary distinction between diffusive and chemical equilibrium in this case is the importance or significance of any energy transferred by collisions.

The importance of collision processes decreases progressively as altitude is increased in the mesosphere. Thus, chemical reactions requiring large energy accommodations by three-body collisions become

less and less probable as altitude increases in the mesosphere. This factor is particularly helpful in selecting probable chemical or kinetic reactions in the vicinity of 85 Km or higher.

Downward diffusion of atomic or molecular hydrogen requires some chemical or kinetic mechanism to overcome the normal tendency for hydrogen to diffuse upward by virtue of its small mass. One possible mechanism involves the electrostatic forces exerted on hydrogen by oxygen atoms. Atomic hydrogen and oxygen have nearly identical ionization potentials, 13.59 eV and 13.61 eV respectively. This means that the asymmetric resonance reaction

$$H^+ + 0 \rightleftarrows H + 0^+ \tag{9}$$

requires an energy accommodation of about 0.02 eV. This value of 0.02 eV is by far the lowest energy accommodation level of all the possible reactions considered and, given a sufficient quantity of atomic oxygen, this reaction may provide a substantial source and sink for hydrogen atoms.

Atomic oxygen is formed in the mesosphere by photodissociation of molecular oxygen during daylight hours [14].

$$0_2 + h\nu \rightarrow 0 + 0 \tag{10}$$
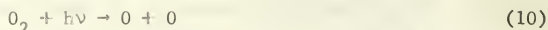
Below about 95 Km, oxygen atoms recombine about as fast as they are photodissociated and a condition of photo-chemical equilibrium exists. The most important destruction mechanisms for atomic oxygen are

$$0 + 0 + M \rightarrow 0_2 + M \tag{11}$$

$$0 + 0_2 + M \rightarrow 0_3 + M . \tag{12}$$
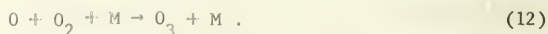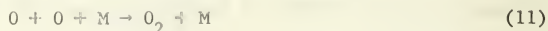
Atomic oxygen also forms at even greater altitudes, i.e. above 100 Km, where its recombination lifetime is of the order of several months. These oxygen atoms diffuse downward and recombine at altitudes below

100 Km. This downward diffusion characteristic of atomic oxygen is significant in that hydrogen diffusion may also be affected via the resonance reaction, equation 9.

The predicted steady state concentration of atomic oxygen in the mesosphere is shown in Figure 6. The concentration of atomic hydrogen is also shown for comparison, and the quantity of atomic oxygen available in the mesosphere is great enough to make reaction (9) at least plausible. However, in addition to significant hydrogen and oxygen concentration requirements, a relatively large reaction cross-section is necessary to provide a substantial number of resonance reactions. Rapp and Francis [16] have investigated several hydrogen resonance reactions of the forms

$$H^+ + H \rightarrow H + H^+ \tag{13}$$

and

$$H^+ + X \rightarrow H \quad X^+ + \Delta E \tag{14}$$
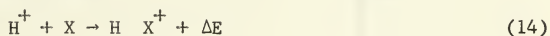
where X is an arbitrary element and ΔE represents the difference in ionization potential between the two species. The reaction cross-section, σ, varies with both proton velocity and ΔE, as shown in Figure 7. The cross-section for reaction (13) is given by the solid (H resonant) line. The cross-section for reaction (14) is always less than or equal to the H resonant cross-section, depending upon the proton velocity and the difference in ionization potential.

Using Figure 7, hydrogen-oxygen resonance may be compared with reaction (15) for moderate proton velocities, i.e. 7×10^5 cm/sec, (or .25 eV) as shown:
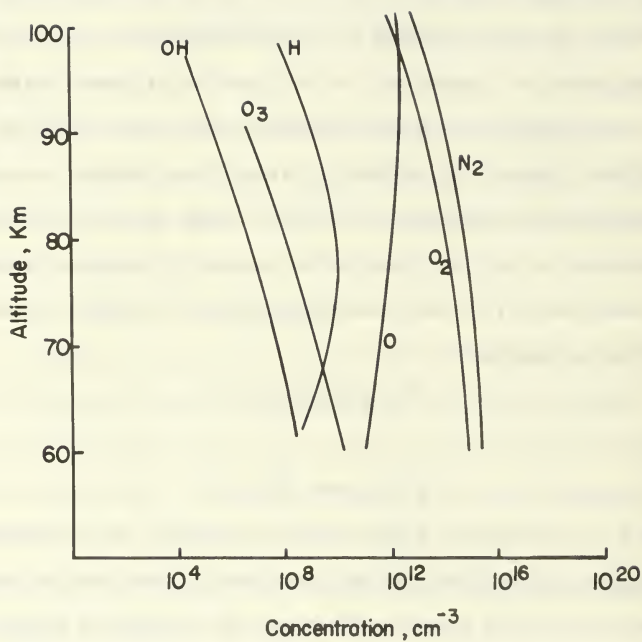
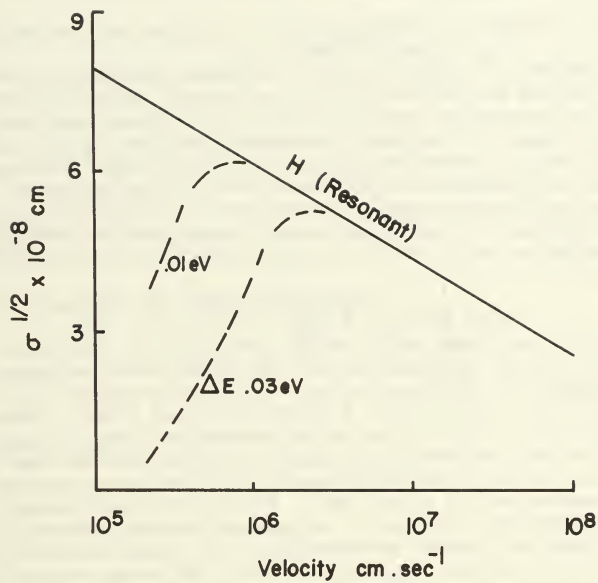FIGURE 6. PARTICLE NUMBER DENSITIES VS.
ALTITUDE (REF. 15)

FIGURE 7. REACTION CROSS-SECTION VS.
PROTON VELOCITY

$$H^+ + H \; (^2S) \rightarrow H \; (^2S) + H^+ \tag{15}$$

$$H^+ + O \; (^3p) \rightarrow H \; (^2S) + O \; (^4S) + .02 \text{ eV} \tag{16}$$
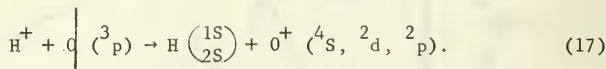
$$\sigma_{15}^{1/2} \approx 7 \times 10^{-8} \text{ cm}$$

$$\sigma_{16}/\sigma_{15} \approx .1.8$$

$$\sigma_{16} = 9 \times 10^{-16} \text{ cm}^2.$$

This cross-section for reaction (16) is relatively large and therefore a substantial number of low energy resonance reactions appear feasible.

Mapleton [17] computed the cross-sections for the following resonance reactions at much higher energy levels than the work of Rapp and Francis [19]:

$$H^+ + O \; (^3p) \rightarrow H \left(\begin{array}{c} 1S \\ 2S \end{array} \right) + O^+ \; (^4S, \; ^2d, \; ^2p). \tag{17}$$

The reported capture cross-section into the H(1S) state was about 3×10^{-16} cm^2 for O^+ (^4S, ^2d) at a proton energy of 40 KeV. The value for O^+ (^2p) at both the same proton energy, 40 KeV, and the same H(1S) state was reported as 1.7×10^{-16} cm^2. For higher proton energy levels of about 125 KeV the capture cross-sections for the H(1S) state decreased by a factor of six or seven. Cross-sections for H(2S) were reportedly one order of magnitude less than those for the corresponding H(1S) states.

The kinetics of these resonance reactions is important in determining diffusion characteristics of the overall hydrogen-oxygen complex. Above proton energy levels of 50 KeV, the protons travel through the mesosphere, rapidly losing kinetic energy and causing secondary ionization of ambient molecules. However, once below 50 KeV, protons can induce electro-static potentials in oxygen atoms that exactly balance the kinetic energy of relative motion. A quasi-stationary two-body orbit then results, whose lifetime is sufficient to permit charge transfer or

resonance to occur. This process is generally expressed in terms of the capture cross-section versus the loss cross-section. In this case the two are approximately equal at 50 KeV, with the capture cross-section predominating below 50 KeV.

These reported resonance cross-sections for protons with energies of 50 KeV or less indicates that such resonance reactions are important whenever a sufficient quantity of atomic oxygen is available. The reaction cross-sections are large enough to compensate for the fact that hydrogen and atomic oxygen are minor constituents of the 70 Km to 100 Km region. This indicates that proton resonance with atomic oxygen is a competitive if not dominant reaction in the 70 Km to 100 Km region following periods of proton bombardment.

In addition to the atomic oxygen-proton reactions discussed above, molecular oxygen resonance may also be important in subsequent reactions involving the excited hydrogen atoms which escape 0-H resonance. E.C.Y. Inn [18] has proposed the following resonance transfer process as the most effective quenching mechanism for excited hydrogen atoms with a total quantum number $n \geq 3$ (i.e, H* with excitation energies $\geq$ 12 eV).

$$H^* + O_2 \rightarrow H + O_2^+ + e \tag{18}$$
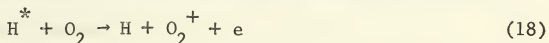
The number of ion-pairs, qs, in the region of 60 - 70 Km is conservatively estimated as 3.6 ion-pairs cm^{-3} sec^{-1} based on observed levels of electromagnetic absorption during proton bombardment. Assuming these ion-pairs occur due to an effective hydrogen flux, F, at 70 Km gives the following relation:

$$F \times \sigma_R = \frac{qs}{n(O_2)} \tag{19}$$

where σ_R is the reaction cross-section and $n(O_2)$ is the molecular oxygen density at 70 Km. Inn assumed that for each fast proton 60

quanta of H_α are emitted, and he obtained an estimate of the excited
hydrogen flux

$$F = 1.5 \times 10^5 \text{ cm}^{-2} \text{ sec}^{-1}$$

and

$$\sigma_R = 6 \times 10^{-20} \text{ cm}^2.$$

The above discussions indicate that atomic and molecular resonance
reactions provide a significant means for concentrating atomic or
molecular hydrogen in the mesosphere. Furthermore, the tendency for
atomic hydrogen to diffuse out of the region by virtue of its smaller
mass is also reduced by the effects of the larger oxygen mass when in
resonance. The net result is the accumulation of a substantial number
of protons with energies in the low KeV range, plus an increased
number of other ionic species as a result of secondary ionization from
proton bombardment. This excited state can in turn be supported or
maintained by a solar radiation primarily in the ultra-violet wave
lengths.

III. RELAXATION MECHANISMS IN THE MESOSPHERE

A. GENERAL DISCUSSION

Section II described how energetic protons could excite the 70 Km to 100 Km region, and also mentioned how this excited state could be supported or maintained by solar radiation. Section III now describes how various hydrogen-oxygen relaxation reactions could occur as the entire region cools and contracts in the absence of solar radiation. The first relaxation reactions to occur are primarily ion-ion recombinations. This in turn is followed by molecular reactions and then possibly by phase changes as the region approaches its lowest energy state. Finally, a possible energy cycle will be considered which incorporates these relaxation reactions.

B. ION-ION RECOMBINATION

When the solar radiation has ended at local sunset (approximately 30 minutes after surface sunset) ambient conditions change to the point where two-body reactions such as electron attachment and ion-ion recombination become important.

Electron attachment to oxygen occurs readily in the mesosphere. This is shown by the relatively large values of electron affinity, EA, exhibited by oxygen

$$EA \ (O) = 1.465 \pm .005 \ eV,$$

$$EA \ (O_2) = 0.15 \pm 0.05 \ eV.$$

However, such electrons are easily detached by almost every form of visible light, as expressed by the photodetachment rate, ρ.

$$\rho \ (0^-) = 1.4 \ \text{sec}^{-1}$$

$$\rho \ (0^-_2) = .44 \ \text{sec}^{-1}.$$

Since atomic oxygen decreases somewhat steadily after sunset by recombination, the most favorable period for a large concentration of 0^- occurs just after sunset.

As previously discussed, in the case of proton resonance with neutral atomic oxygen the relative kinetic energy exactly balanced an induced electrostatic force in the oxygen. This resulted in a minimum radius or potential energy barrier that prevented any further reaction. This potential energy barrier is greatly reduced if the oxygen atom is negatively charged. The orbital radius is much smaller and the probability of further reaction increases. This leads to ion-ion recombinations of the form

$$H^+ + 0^- \rightarrow OH* \ . \tag{20}$$
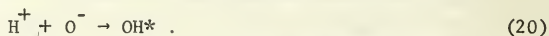
Such a reaction would permit the direct conversion of energetic protons into excited OH radicals. Collisional deactivation of such excited OH radicals could play an important part in the total energy balance of the region. Large quantities of the proton energy accumulated over a period of hours could be radiated out of the region in the order of several minutes.

C. RELAXATION BY CHEMICAL REACTION AND BY CONDENSATION

An increase in the OH concentration in the mesosphere is important not only because of the sudden relaxations occurring from excited electronic states, but also for the subsequent chemical reactions as well. Reactions involving OH radicals may possibly cause supersaturation of the mesosphere by water vapor or by hydrogen peroxide vapor. Two-body

gas phase reactions may produce the water or hydrogen peroxide vapors, but the lack of suitable surfaces or condensation nuclei may prevent any lower phase, as expected for thermal equilibrium. Such a metastable condition could persist indefinitely, but any further change in state would cause the supersaturated state to collapse by condensation. The collapse of a metastable state is a relaxation process similar to chemical reaction. Such a collapse could be induced by a shock wave disturbance or by introduction of numerous condensation nuclei from rocket exhausts or vehicle ablation.

Hydrogen peroxide appears to offer the highest degree of super-saturation throughout the mesosphere, since the temperatures of the region are well below the estimated sublimation points for hydrogen peroxide. The chemistry of the mesosphere is such that hydrogen peroxide products may be an intermediate step in the formation of water or ice. The hydrogen peroxide products result from the fact that water reactions are complex, with many intermediate steps. These individual steps often require a suitable third body to provide the necessary adjustability in energy and momentum to complete the reaction. The final steps in these reactions usually require the largest energy accommodations and may therefore be suppressed if a suitable third body is not available. The most important third-body characteristic in this case is sufficient surface area to permit rapid thermal radiation of the energy transferred by this reaction. The particle density and size in the upper half of the mesosphere may preferentially support the formation of hydrogen peroxide instead of water. For these reasons hydrogen peroxide may be a potential factor in supersaturation of the upper regions of the mesosphere.

There is some physical evidence of such molecular reactions in the mesosphere; however, it is difficult to detect water vapor or hydrogen peroxide vapor in the mesosphere by the technique of measuring the absorption characteristics of the region. This is especially true if such measurements are made from the surface of the earth. The use of balloon-borne spectrometers combined with a satellite laser source may provide sufficiently accurate data for positive identification sometime in the near future. There is some evidence available from STRATASCOPE II which may be significant in this respect. STRATASCOPE II involved spectrographic measurements of various planets and stars from an altitude of 30 Km above the earth's surface. Although the water absorption so observed is generally attributed to the star or planet atmosphere concerned, assuming water absorption by the earth's atmosphere above 30 Km to be negligible, STRATASCOPE II indicated such an assumption may not be appropriate when the mesosphere is not in thermodynamic equilibrium since water vapor may be present.

Cloud formations have been observed in the mesosphere following proton excitation. The existence of these clouds supports some type of molecular reaction and relaxation. Recoverable rocket probes have been utilized to obtain particle samples from cloud formations observed in the mesosphere. These cloud formations have distinct characteristics in terms of their visible emissions and appearance. They are generally known as optical aurora or noctilucent clouds. The particles recovered from these noctilucent clouds are basically micrometeorities or inter-planetary dust particles consisting of iron and nickel. The particles ranged in diameter from 2×10^{-6} cm to 6×10^{-5} cm over an altitude range of 75 Km to 98 Km. Electron microphotography [19] studies of the

sampler's calcium surfaces revealed that virtually all particles with diameters greater than 1.7×10^{-5} cm had distinct haloes attributed to a water reaction with the calcium surface. Thus, these larger particles reportedly served as condensation nuclei in some form of water reaction.

There are several reasons to suspect that hydrogen peroxide or even higher peroxide radicals are involved in some crystal formations in addition to water. First, all of these substances produce water when heated. Secondly, the physical characteristics [20] of the addition compound $H_2O_2 \cdot 2H_2O$ appear more suitable to the mesospheric conditions. The freezing points of a 40% to 60% mixture of $H_2O_2 \cdot 2H_2O$ are roughly 50 K less than either water or anhydrous hydrogen peroxide. The higher radicals [21] such as H_2O_4 exist only at even lower temperatures, i.e., 150 K. Such substances appear more compatible with the maximum and minimum temperatures observed in the mesosphere during periods of noctilucent cloud activity (see Figures 8 and 9).

Additionally, the observed color or chromaticity [22] of noctilucent clouds does not indicate that these clouds consist solely of water vapor or ice. Clouds that consist solely of water vapor have a white color, and pure ice crystals display all the colors of the rainbow by reflecting sunlight. On the other hand, noctilucent clouds never become irridescent; instead, they show an azure-blue tint. This color characteristic indicates that some substance other than water vapor takes part in the process of condensation or crystallization. Ozone [Ref. 22, p. 117] has been mentioned as a possible substance. However, Spring [23] has reported that anhydrous hydrogen peroxide acquires a color through scattering sunlight described as blue with a nuance of green.
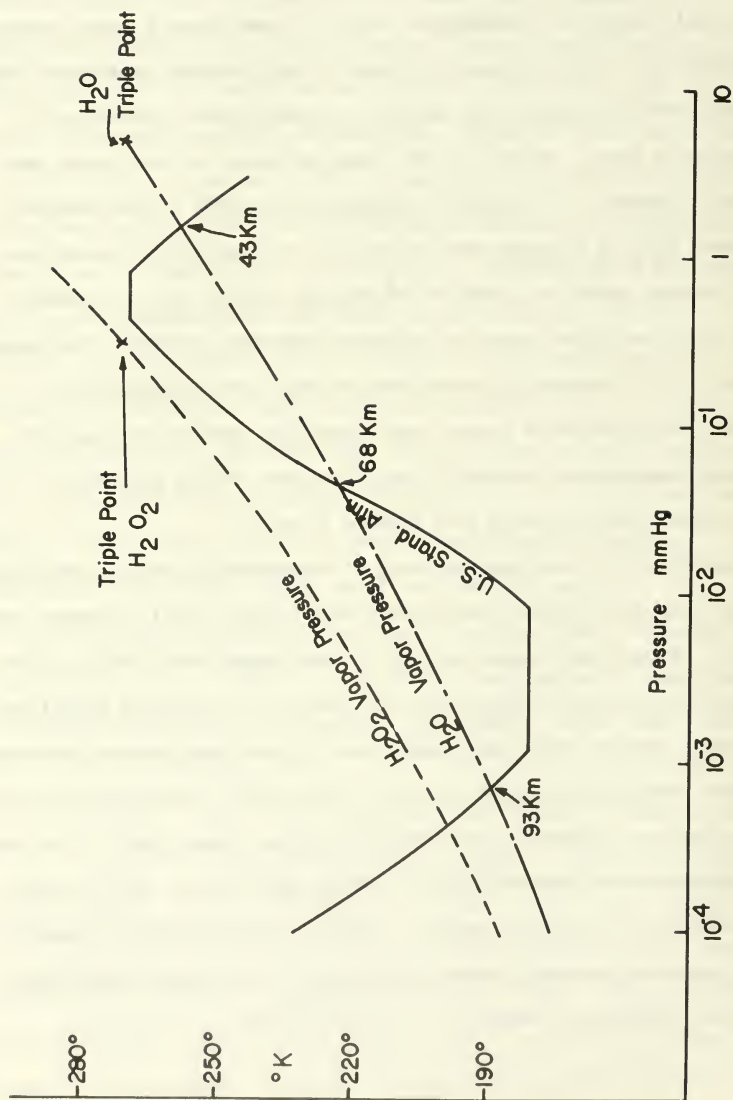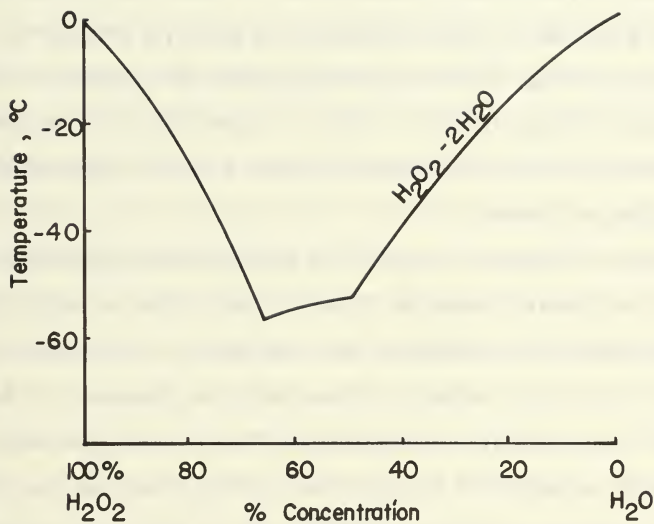
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FIGURE 8. MESOSPHERE TEMPERATURE AND PRESSURE

FIGURE 9. FREEZING POINTS OF $H_2O_2 - 2H_2O$ MIXTURES
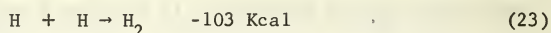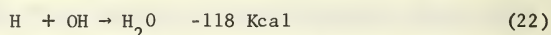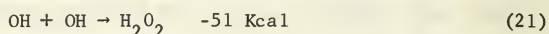(REF. 23, p.211)

The fact that these clouds exist at mesospheric levels indicates the feasibility of supersaturation reactions. Other factors, such as the extremely low temperatures required (150°K to 170°K), an increase in OH emission intensity, plus an apparent correlation with proton and electron bombardment, tend to support an OH reaction of some form. Finally, noctilucent clouds usually appear during the summer months, indicating that long periods of solar irradiation are generally followed by extremely low temperatures in the mesosphere. This suggests a relaxation mechanism involving radiation cooling. However, all of these factors combined are still not sufficient to permit a positive identification of the mechanism involved.

There are a number of possible OH electro-chemical reactions which lead to the eventual formation of water. None of the molecular compounds formed by these reactions are very stable in the presence of intense ultra-violet radiation. These molecular compounds, in decomposing, usually absorb large quantities of solar energy and become excited OH radicals. So in this sense, such compounds can eventually lead to radiation cooling and crystal formation after long periods of exposure to intense ultra-violet radiation. This agrees well with the observed conditions required for noctilucent cloud formation. Also, the phase characteristics of some of these compounds, particularly mixtures of peroxide radicals, appear compatible with the low temperature extremes reported in the mesosphere during noctilucent cloud activity. The basic remaining question concerns the types and feasibility of OH reactions that could produce hydrogen peroxide or higher peroxide radicals.

Since water vapor is an end product of all the reactions considered, the destruction of water vapor is important, particularly if some OH is being continually resupplied to the mesosphere via such reactions as water decomposition. Ultra-violet radiation has already been mentioned as a means of water decomposition into H and OH. Small quantities of hydrogen peroxide may also be produced by this irradiation [24]. However, a much more important process for hydrogen peroxide production involves high energy proton bombardment of water vapor [25]. Normally the direct combination of two OH radicals to form one hydrogen peroxide molecule is very difficult to achieve in the presence of H_2O or water, unless the concentration of OH is unusually high. High energy protons produce the high OH concentrations necessary for bimolecular association into hydrogen peroxide. The high OH concentration results from proton collisions with water molecules. A hydrogen atom is forcibly dislodged from the water molecule so that it travels a great distance from the proton's path and any chance for recombination with the OH radical is greatly reduced. As the proton energy increases, the probability of bimolecular association of OH radicals also increases. Hydrogen peroxide yields of up to 30% have been reported for proton energies in the 6 to 7 MeV range. Since such high energy protons appear frequently in the mesosphere this process appears feasible as a source of hydrogen peroxide.

Electrical discharges [26] in a low pressure gas containing saturated water vapor will produce a large population of OH radicals as indicated by the fluorescent clouds produced. In most cases the water vapor immediately condenses on the electrons and ions formed by the discharge, with little or no net formation of hydrogen peroxide. If, however, the number of electrons discharged is sufficiently great enough to provide

complete dissociation into hydrogen and OH radicals, hydrogen peroxide
yields of up to 60% are possible. The maximum yield reportedly occurs
at a water vapor pressure of 0.1 to 0.2 mmHg, which corresponds to an
altitude range of 68 to 65 Km. The composition of the final products
depends upon the relative degree to which the following three competing
reaction occur

$$OH + OH \rightarrow H_2O_2 \quad -51 \text{ Kcal} \tag{21}$$

$$H + OH \rightarrow H_2O \quad -118 \text{ Kcal} \tag{22}$$

$$H + H \rightarrow H_2 \quad -103 \text{ Kcal} \tag{23}$$

The type of surface, and the surface temperature, are the controlling
factors for the above reactions. In the mesosphere these surfaces are
primarily micrometeorites consisting of iron and nickel. The surface
temperatures of these particles is probably well below the ambient gas
temperature, once sunset occurs. Surface temperature is important in
that reaction (21) is virtually negligible at temperatures above $200^{\circ}K$.
Since the reactions shown above are general in nature, they are not
restricted to an electrical discharge process. These equations apply
to any suitable concentration of H or OH plus a sufficient number of
micrometeorites to accommodate the energy released by the particular
reaction. In this sense a small micrometeorite surface area tends to
inhibit relatively higher energy reactions such as reactions (22) and
(23). Under such circumstances as those reported for the vicinity of
85 Km, reaction (21) appears somewhat more probable than reactions (22)
and (23).

Hydrogen and oxygen react in a complex manner to produce water.
Hydrogen peroxide is formed as an intermediate step for temperatures
and pressures comparable to those of the mesosphere. For hydrogen

peroxide to remain as a somewhat stable product requires that the final steps in this water reaction be suppressed. The overall reaction is quite complex involving the formation and disappearance of such species as OH, HO_2 and H_2O_2 by a large number of simultaneously and successively occurring reactions. The relative importance of each reaction varies significantly with such factors as temperature, pressure, and concentration of hydrogen plus the physical and chemical nature of the surfaces exposed. In the upper regions of the mesosphere, around 85 Km, these factors appear suitable for the formation of the addition compound $H_2O_2 \cdot 2H_2O$, mainly based on the assumption that water formation cannot be completely suppressed even at this altitude.

D. PROPOSED MESOSPHERE ENERGY CYCLE

The formation of a solid substance such as frozen peroxide radicals or even crystals of $H_2O_2 \cdot 2H_2O$ from the various sources of OH radicals could be one phase of a general energy cycle involving the short term storage of solar energy during daylight hours and the subsequent conversion to thermal energy during the dark hours in the mesosphere. The temperature inversion between 65 Km and 85 Km provides an upward convection of warm gases such as hydrogen and OH radicals. These gases would be provided by the gradual decomposition of falling peroxide crystals as they encounter an ever-increasing level of atmospheric ozone. Such a cycle is shown in Figure 10.
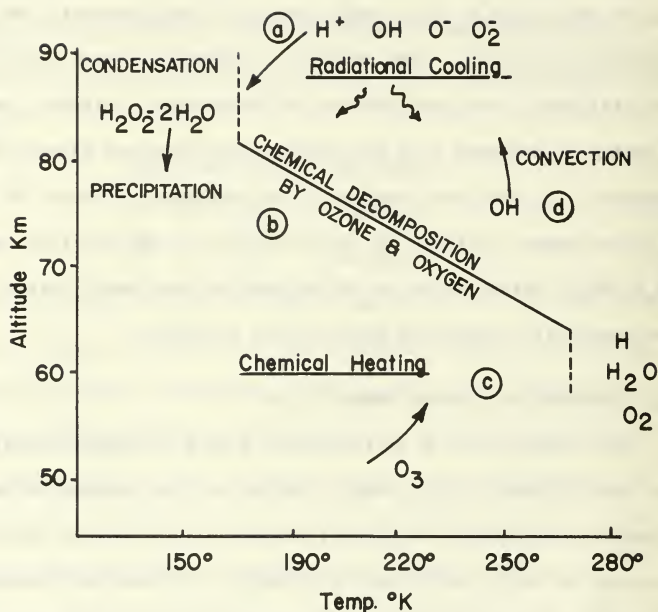
a. RADIATIONAL COOLING LEADS TO CONDENSATION REACTIONS PRODUCING $H_2O_2 \cdot 2 H_2O$

b. $H_2O_2 \cdot H_2O$ PRECIPITATES TO LOWER & WARMER ALTITUDES SLOWLY DECOMPOSING WATER COMPONENT

c. RAPID DECOMPOSITION OF REMAINING H_2O_2 BY OZONE

d. CONVECTION OF GASEOUS PRODUCTS

FIGURE 10. HYDROGEN-OXYGEN ENERGY CYCLE

A. GENERAL DISCUSSION

The preceding discussion of energy storage mechanisms in the mesos-
phere indicate that at times this altitude region may reach a state of
non-equilibrium that is unparalled in any other portion of the earth's
atmosphere. Normally volumetric expansion or contraction of the
mesosphere plays a principal role in governing the rate of return to
equilibrium, or in initiating some relaxation mechanism. However, it
seems equally possible that a space vehicle on its way through the
mesosphere might also trigger similar reactions. This could in turn
lead to reversals in the expected transfer of kinetic and thermal
energy from the vehicle to the surrounding environment.

It is virtually impossible to consider the effects of various
simulatneous and successively occurring reactions as a whole. There-
fore some of the more unusual effects will be considered independently.

B. SHOCK EFFECTS ON SPACECRAFT OPERATION

The most noticeable characteristic of the mesosphere is its
temperature profile and the large negative gradient between 65 Km
and 85 Km between two isothermal regions. Extensive shock wave
reflections can occur as a result, and widespread shock induced
relaxation reactions may lead to operational difficulties. Shock waves
propagating through this region tend to collect and concentrate the
lighter particles such as hydrogen atoms and electrons in the region
immediately behind the shock front. This higher concentration of
hydrogen and electrons tends to increase relaxation reactions of the

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types previously discussed. Also the shock front itself may provide a suitable surface for three-body type relaxation mechanisms that are normally inhibited by the lack of an energy absorbing surface. Such relaxation reactions, particularly ones involving hydrogen, could substantially increase radiation intensity levels in the region. These high radiation levels could persist for several minutes due to a confining force exerted by the earth's magnetic field. The overall effect on spacecraft operation would mainly be electromagnetic blackout of communications or radar tracking equipment. In cases where slow moving blunt bodies are involved, radiation heat loads may become a problem.

C. DRAG EFFECTS

The interaction of an electrically charged space vehicle with an ionized atmosphere could lead to substantial changes in pressure distribution around the vehicle. A large negative charge on a vehicle surface will deflect ions away from forward stagnation points and will then attract these same ions into the vehicle wake region. This ionic force tends to equalize the forward and aft stagnation pressures causing an overall decrease in pressure drag [27]. The electrical energy required to maintain this ionic action must be supplied by high energy electrons collected on the vehicle surface.

NASA [28] has conducted work of this nature utilizing a controllable onboard magnetic field to couple with the ion flow as opposed to the electrostatic field mechanism mentioned above. The pressure drag in this case also changed significantly, but total drag reportedly remained constant due to the appearance of a lateral electrical drag force. These lateral forces could possible be used to control a vehicle's flight path in a highly ionized environment.

A reduction in pressure drag due to ion deflection away from the forward stagnation point and into the wake could cause excessive heating of the vehicle's base surfaces. However the most important operational effect appears to be the increase in wake relaxation reactions that would follow. The use of vehicle surface materials that are chemically inert with respect to hydrogen and oxygen may prove helpful in reducing wake reactions. This could also be accomplished through the use of special wake suppressant materials or possibly by water injection into the wake. The use of such materials would serve to absorb the excessive energy and accelerate the relaxation reaction rates.

D. RADIO FREQUENCY EFFECTS

Radio frequency absorption or reflection in the mesosphere can present severe operational problems in terms of communication and radar tracking equipment performance. The high electron and ion densities normally encountered in the mesosphere are greatly increased by many of the physical and chemical disturbances associated with a typical vehicle penetration of the region. Electron densities associated with normal night-time and day-time conditions as well as the electron densities predicted for various vehicle velocities are shown in Figures 11 and 12. The natural or resonant absorption frequency [29] is dependent upon this value of electron density as shown by the following expression

$$f_c^2 = \frac{N\,e^2}{4\pi^2\,\varepsilon_o\,m} = 8I\ N \tag{24}$$

where
N = number of electrons/cm^3,
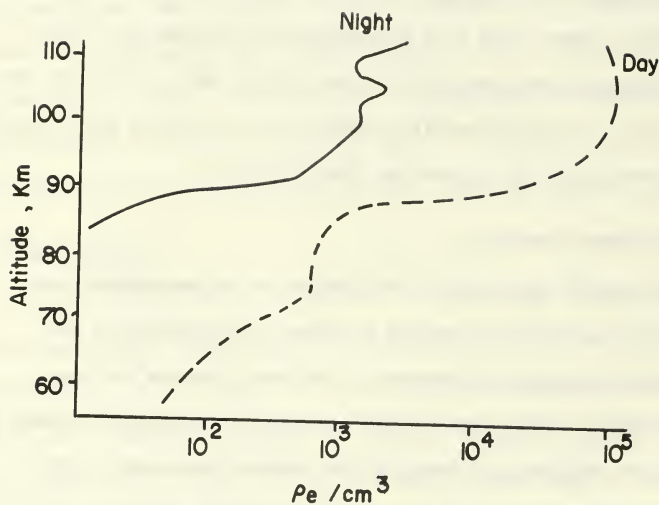
e = charge of an electron,

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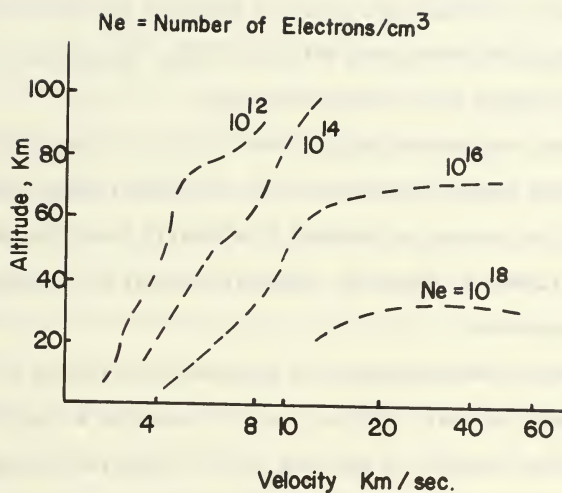FIGURE II. ELECTRON DENSITY VS. ALTITUDE
(REF. 7, p.53)

FIGURE 12. STAGNATION POINT ELECTRON DENSITY
VS. VEHICLE VELOCITY (REF. 30)

m = mass of an electron,

ϵ_o = dielectric constant of free space.

Thus, a signal transmitted at this critical frequency will be totally reflected from an altitude where the electron density is equal to the following value

$$N = f_c^2/8I. \tag{25}$$

All frequencies less than this critical frequency are reflected back toward the transmitter altitude while all higher frequencies continue to propagate through this critical altitude.

Similarly, transmission through shock fronts or other locally ionized regions usually requires the use of extremely high frequencies. For example, the ionization produced by a vehicle travelling at 8 Km/sec and at an altitude of 70 Km will completely reflect all frequencies up to several giga Hertz.

The effects of RF abosroption or blackout are difficult to overcome, but again the basic problem is one of quenching a highly reactive gas, or possibly of avoiding vehicle operation during periods or in areas where such highly excited states may be expected. In this respect early morning operations appear more favorable than late afternoon or early evening operations. It also appears that high magnetic latitudes should be avoided whenever possible. These high latitudes are areas of extreme field convergence which could be easily disturbed by most types of vehicle operations during periods following proton excitation.

V. POTENTIAL APPLICATIONS OF MESOSPHERIC ENERGY

Any practical application of mesospheric energy will depend upon the final answers to such questions as: "How much energy is generally available at any given time, or how much energy can be stored in a given region?"; "How fast is the region returned to equilibrium from a specific energy level and how can this rate be varied or controlled?". It is conceivable that the answers to these questions could lead to new types of propulsion systems which exploit the possibility of reduced drag, plus the availability of hydrogen-oxygen compounds as supplemental fuel. Water may also someday be obtained from the mesosphere either as a combustion by-product, or from a special conversion unit on board the spacecraft. Mesospheric energy may also find defensive applications such as the possible screening of surface areas from possible electronic surveillance by orbiting space stations. It may also be possible to artificially form a temporary thermal barrier to protect against offensive missile threats. However, at the present time it is impossible to make any definite assessment of the region's true potential in any of these areas.

VI. SUMMARY

The available experimental evidence suggests that some form of energy storage mechanism involving energetic particles such as protons and electrons from the solar wind periodically acts in the mesosphere. It has been further proposed that this mechanism is primarily dependent upon hydrogen-oxygen resonance as an energy storage element. It has also been proposed that definite energy relaxation mechanisms are involved which tend to maintain or prolong the total energy storage capacity of the 70 Km to 100 Km altitude region. The basic function of this proposed energy cycle is to moderate incoming solar energy in a manner that is most easily accommodated by lower regions of the atmosphere, i.e., radiation in the water bands, and the formation of hydrogen-oxygen compounds such as $H_2O_2 \cdot 2H_2O$.

The possible effects of such an energy cycle on spacecraft operations have been briefly considered particularly with regard to vehicle-induced total or partial relaxation. Operational alternatives were proposed to minimize undesirable effects of such self-induced relaxation reactions. Finally, a few potential applications of such an energy source were mentioned.

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13. ABSTRACT

Hydrogen and oxygen reactions in the earth's atmosphere between 70 Km and 100 Km may at times serve as a relaxation mechanism for this region of the atmosphere. Energy stored in this region as a result of intense solar radiation, or energetic particle bombardment, may be rapidly released by hydrogen-oxygen reactions. Such reactions include ion-ion recombination and condensation of supersaturated mixtures of water or hydrogen peroxide vapors in the region.

The possible nature of such mechanisms was considered in an attempt to estimate the effects on spacecraft performance in this altitude region. The basic question involved was whether the chemical and kinetic energy stored in hydrogen-oxygen complexes could materially affect spacecraft performance.

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Proton excitation						
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Wake formations						